Steric Effects in Electrolytes: A Modified Poisson–Boltzmann Equation

Itamar Borukhov and David Andelman

School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel

Henri Orland

Service de Physique Théorique, CE-Saclay, 91191 Gif-sur-Yvette, Cedex, France

The adsorption of large ions from solution to a charged surface is investigated theoretically. A generalized Poisson–Boltzmann equation, which takes into account the finite size of the ions is presented. We obtain analytical expressions for the electrostatic potential and ion concentrations at the surface, leading to a modified Grahame equation. At high surface charge densities the ionic concentration saturates to its maximum value. Our results are in agreement with recent experiments.

The interaction between charged objects (interfaces, colloidal particles, membranes, etc) in solution is strongly affected by the presence of an electrolyte (salt) and is of great importance in biological systems and industrial applications [1,2]. The main effect is screening of the Coulomb interaction characterized by the so-called Debye–Hückel screening length [3], which depends on the ionic strength of the solution. The Deryaguin-Landau-Verwey-Overbeek theory, based on the competition between screened Coulomb and attractive van der Waals interactions, has been very successful in explaining the stabilization of charged colloidal particles [4].

One of the most widely used analytical method to describe electrolyte solutions is the Poisson–Boltzmann (PB) approach [5]. For low electrostatic potentials (less than 25 mV), the PB equation can be linearized and yields the Debye-Hückel theory [3]. The PB is a continuum mean-field like approach assuming point-like ions in thermodynamic equilibrium and neglecting statistical correlations. This theory has been successful in predicting ionic profiles close to planar and curved surfaces and the resulting forces. However, it is known to strongly overestimate ionic concentrations close to charged surfaces. In particular, this shortcoming of the PB theory is pronounced for highly charged surfaces and multivalent ions.

Since the PB equation does not take into account the finite size of the adsorbing ions, the ionic concentration close to the surface can easily exceed the maximal allowed coverage by orders of magnitude. Several attempts have been proposed to include the *steric* repulsion in order to improve upon the PB approach [6,7]. One of the first attempts to incorporate steric effects is the *Stern layer* modification [6,8] of the PB approach. Steric effects are introduced by excluding the ions from the first molecular layer close to the surface. However, it seems difficult to improve on this method in a systematic way. More recent modifications [6,7,9–11] rely either on Monte Carlo computer simulations or on numerical solutions of integral equations (the "hypernetted chain" equation [9]). These approaches involve elaborate numerical calculations and lack the simplicity of the original PB approach.

In this Letter, we propose a simple way to include steric effects in the original PB approach. This modified PB equation clearly shows how ionic saturation takes place close to a charged surface. The equation is derived for 1:z asymmetric and z:z symmetric electrolytes. At low ionic concentration, the original PB equation is recovered. Simple analytical relations between the surface charge density and the counterion concentration at the surface are obtained, in agreement with recent experiments [12].

Consider an asymmetric electrolyte consisting of negative multivalent ions of charge $-ze$, and positive monovalent ions of charge e, where e is the electron charge. The bulk concentration of the negative and positive ions is c_b and zc_b, respectively, as implied by charge neutrality.

Within mean–field approximation, the total free energy, $F = U - TS$, can be written [13] in terms of the local electrostatic potential $\psi(\mathbf{r})$ and the ion concentrations $c^\pm(\mathbf{r})$. The electrostatic energy contribution U is:

$$U = \int \mathrm{d}\mathbf{r} \left[-\frac{\varepsilon}{8\pi}|\nabla\psi|^2 + ec^+\psi - zec^-\psi \right.$$
$$\left. -\mu_+ c^+ - \mu_- c^- \right] \tag{1}$$

The first term is the self energy of the electric field, where ε is the dielectric constant of the solution. The next two terms are the electrostatic energies of the ions, and the last two terms couple the system to a bulk reservoir, where $\mu_\pm$ are the chemical potentials of the ions. The entropic contribution $-TS$ is

$$-TS = \frac{k_B T}{a^3} \int \mathrm{d}\mathbf{r} \left[c^+ a^3 \ln(c^+ a^3) + c^- a^3 \ln(c^- a^3) \right.$$
$$\left. + \left(1 - c^+ a^3 - c^- a^3\right) \ln\left(1 - c^+ a^3 - c^- a^3\right) \right] \tag{2}$$

where $k_B T$ is the thermal energy. For simplicity, we assume that both types of ions have the same size a. The first two terms are the entropies of the positive and negative ions, whereas the last term is the entropy of the solvent molecules. Indeed, this last term is responsible for the novel steric corrections to the PB equation. In a more rigorous way, these corrections are obtained by considering a lattice-gas version of the Coulomb gas in which each lattice site is occupied at most by one ion [14].

The variation of the free energy $F = U - TS$ with respect to ψ and $c^{\pm}$ yields our modified PB equation for the 1:z electrolyte:

$$\nabla^2 \psi = -\frac{4\pi}{\varepsilon}\left[ec^+(\mathbf{r}) - zec^-(\mathbf{r})\right]$$
$$= \frac{4\pi zec_b}{\varepsilon} \frac{e^{z\beta e\psi} - e^{-\beta e\psi}}{1 - \phi_0 + \phi_0(e^{z\beta e\psi} + ze^{-\beta e\psi})/(z+1)} \tag{3}$$

where $\phi_0 = (z+1)a^3 c_b$ is the total bulk volume fraction of the positive and negative ions.

For a symmetric z:z electrolyte, one gets

$$\nabla^2 \psi = \frac{8\pi zec_b}{\varepsilon} \frac{\sinh(z\beta e\psi)}{1 - \phi_0 + \phi_0 \cosh(z\beta e\psi)} \tag{4}$$

where $\phi_0 = 2a^3 c_b$. In the limit of small ionic concentrations, $\phi_0 \to 0$, Eqs. 3,4 reduce to the standard PB equations. Moreover, for any ionic concentration and at low electrostatic potentials, $|\beta e\psi| \ll 1$, both equations reduce to the linearized PB equation (Debye-Hückel limit) $\nabla^2 \psi = \kappa^2 \psi$ where κ^{-1} is the Debye–Hückel screening length. For the asymmetric case $\kappa^2 = 4\pi l_b z(z+1)c_b$, where $l_b = e^2/\varepsilon k_B T$ is the Bjerrum length equal to 7 $\mathbf{r}$A for aqueous solutions at room temperature.

Our approach deviates significantly from the original PB equation for large electrostatic potentials $|\beta e\psi| \gg 1$. In particular, the ionic concentration is unbound in the standard PB approach, whereas here it is always bound by $1/a^3$ ("close packing") as can be seen from Eqs. 3,4. This effect is important close to strongly charged surfaces immersed in an electrolyte solution.

Note that for high positive potentials, $\beta e\psi \gg 1$, the contribution of the positive ions is negligible and the negative ion concentration follows a distribution reminiscent of the Fermi-Dirac distribution [15],

$$c^-(\mathbf{r}) \to \frac{1}{a^3} \frac{1}{1 + (z+1)\frac{1-\phi_0}{\phi_0}e^{-z\beta e\psi}} \tag{5}$$

where the excluded volume interaction plays the role of the Pauli principle.

To demonstrate the usefulness of our method, we study the case of a single planar surface with charge density $\sigma > 0$ in contact with an electrolyte solution. Ionic concentration profiles are obtained from the numerical solution of Eq. 3 as a function of x, the distance to the

positively charged surface. Since the positive ion concentration is small near the surface, we show in Fig. 1a only the negative ion profiles, as well as the corresponding original PB profile. The main effect is the saturation of the ionic concentration in the vicinity of the charged surface. This should be contrasted with the original PB scheme which leads to extremely high and unphysical values of $c_s^- \equiv c^-(0)$, especially for multivalent ions. In the saturated region, the ionic concentration tends to $1/a^3$, leading to more pronounced deviations from PB for large ions.

In the saturated layer the right–hand side of Eq. 3 becomes a constant, and the electrostatic potential is quadratic

$$\psi(x) \simeq \psi_s - \frac{4\pi\sigma}{\varepsilon}x + \frac{2\pi ze}{\varepsilon a^3}x^2 \tag{6}$$

where ψ_s is the surface potential and the boundary condition $\psi'|_s = -4\pi\sigma/\varepsilon$ is satisfied. As can be seen in Fig. 1b, the parabolic profile of $\psi(x)$ is a good approximation close to the surface. The width of the saturated layer l^* is not strictly equal to a. It can be easily estimated from Eq. 6 to be $l^* \simeq a^3\sigma/ze$ in agreement with Fig. 1a.

The surface potential ψ_s can be calculated in a closed form from the first integral of Eq. 3, assuming that the concentration of the positive ions is negligible at the surface

$$\psi_s = \frac{k_B T}{ze}\left\{\ln\left[e^\zeta - \left(1 - \phi_0\right)\right] - \ln\left(c_b a^3\right)\right\}$$
$$\approx \frac{k_B T}{ze}\left\{\zeta - \ln\left(c_b a^3\right)\right\} \tag{7}$$

where

$$\zeta \equiv \frac{2\pi a^3 \sigma^2}{\varepsilon k_B T} \tag{8}$$

Similarly, the concentration of negative ions at the surface can be calculated leading to a modified Grahame Equation [1]

$$c_s^- = \frac{1}{a^3}\left[1 - (1 - \phi_0)e^{-\zeta}\right] \tag{9}$$

This contribution is depicted in Fig. 2a, where c_s^- is plotted as a function of the surface charge density, σ/e, for two different ion sizes, a. The PB case is shown as well for comparison. At low surface charge $\zeta \ll 1$, the ion concentration reduces to the PB results

$$c_s^- = \frac{2\pi\sigma^2}{\varepsilon k_B T} + (1 + z)c_b \tag{10}$$

but for high surface charge $\zeta \gg 1$, the deviations from the PB case are substantial. Furthermore, as can be seen

from the above equation, the ionic concentration near the surface depends only weakly on the bulk electrolyte concentration, c_b.

In Fig. 2b the ratio between the ion charge density of the first layer $\sigma_1 \simeq zec_s^- a$ and σ is plotted as function of the specific surface area per unit charge, as is often measured in experiments. For the PB approach, this ratio diverges at high surface charge densities (small specific area) because $c_s^- \sim \sigma^2$. However, in our case, the steric effect changes the situation altogether since it prevents the ions from approaching and over-compensating the surface charges.

The theoretical results presented here are relevant to recent experiments [12] where large multivalent ions are adsorbed onto a charged Langmuir monolayer. Large polyanions such as $H_3PW_{12}O_{40}$ (phosphotungstic acid) dissolved in an aqueous subphase are attracted to a cationic Langmuir monolayer such as a fatty amine surfactant ($C_{20}H_{41}$-NH_2), spread at the water/air interface. The adsorbed ion density (per unit area) in the solution, σ_1, is measured by X-ray reflectivity. It is then related to the surface charge density σ, which is controlled by Langmuir trough. The experiments show very clearly the presence of the steric effects for these large ions (of estimated size of 10 **r**A). As the surface charge density increases, σ_1/σ decreases in accord with our findings (Fig. 2b) and in contrast to the original PB approach.

In conclusion, we have derived a modified PB equation including steric effects. As a result the ionic concentration cannot exceed a saturation value of $1/a^3$. This effect is in particular important for large ions adsorbing on charged surfaces. We have obtained analytical expressions for the potential and ion concentrations at the surface. Our results differ qualitatively and quantitatively from the standard PB equation and agree with recent experiments on large polyions in solution.

It would be interesting to further explore the connection between our analytical approach and the Stern layer approach, as well as look at the implications on the forces between two charged planar surfaces.

We wish to thank N. Cuvillier and F. Rondelez for communicating their experimental results to us prior to publication and for useful discussions. We also benefited from discussions and correspondence with H. Diamant, M. E. Fisher, A. A. Kornyshev, P. Sens and M. Urbakh.

[1] J. N. Israelachvili, *Intermolecular and Surface Forces, 2nd ed.* (Academic, London, 1990).

[2] R. J. Hunter, *Foundations of Colloid Science* (Oxford University, New York, 1989).

[3] P. Debye P. and E. Hückel, Physik **24**, 183 (1923); **25**, 97 (1924).

[4] B. V. Derjaguin and L. D. Landau, Acta Phys. Chem. USSR **XIV**, 633 (1941); E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

[5] G. Gouy, J. Phys. (France) **9**, 457 (1910); Ann. d. Phys. **7** 129 (1917); D. L. Chapman, *Philos. Mag.* **25**, 475 (1913).

[6] D. Henderson, Prog. Surf. Sci. **13**, 197 (1983), and references therein.

[7] A. G. Volkov, D. W. Deamer, D. L. Tanelian and V. S. Mirkin, Prog. Surf. Sci. **53**, 1 (1997), and references therein.

[8] O. Stern, Z. Elektrochem. **30**, 508 (1924).

[9] R. Kjellander and S. Marčelja, J. Phys. Chem. **90**, 1230 (1986); R. Kjellander, T. **r**Akesson, B. Jönsson and S. Marčelja, J. Chem. Phys. **97**, 1424 (1992).

[10] P. Attard, D. J. Mitchell and B. W. Ninham, J. Chem. Phys. **88**, 4987 (1988); **89**, 4358 (1988).

[11] B. W. Ninham and V. A. Parsegian, J. Theor. Biol. **31**, 408 (1971); V. A. Parsegian, Trans. Farad. Soc. **62**, 848 (1966).

[12] N. Cuvillier, M. Bonnier, F. Rondelez, D. Paranjape, M. Sastry and P. Ganguly, Progr. Colloid Polym. Sci. **105**, XXX (1997); N. Cuvillier, Ph.D thesis, University of Paris VI, 1997.

[13] I. Borukhov, D. Andelman and H. Orland, Europhys. Lett. **32**, 499 (1995).

[14] I. Borukhov, D. Andelman and H. Orland, (unpublished).

[15] For a similar ionic distribution in solid electrolytes see, e.g., Yu. Ya. Gurevich and Yu. I. Kharkats, Dokl. Akad. Nauk SSSR **229**, 367 (1976) [Sov. Phys. Dokl. **21**, 642 (1976)]. We are indebted to A. Kornyshev for bringing this reference to our attention.

FIGURE CAPTION

Fig. 1: (a) Concentration profiles of negative multivalent ions $c^-(x)$ near a positively charged surface as obtained from the numerical solution of Eq. 3 for two different ion sizes $a = 7.5$ **r**A and $a = 10$ **r**A. Note that the saturated layer width is $l^* \simeq 2$ **r**A and 5 **r**A, respectively. The solid line represents the concentration profile of the standard PB equation. (b) Calculated electrostatic potential profiles near the surface plotted together with the parabolic approximation (Eqs. 6, 7). The dotted, dashed and solid lines are as in (a). The bulk concentration is $c_b = 0.1M$ for a 1:z electrolyte with $z=4$. The surface charge density σ is taken as one electron charge per 50 **r**A^2. The aqueous

solution with $\varepsilon = 80$ is at room temperature.

Fig. 2: (a) Surface concentration of ions as a function of the surface charge density for different ions size, a. The PB concentration is also plotted for comparison. (b) Ratio of the first layer charge density and the surface charge density, $\sigma_1/\sigma = zec_s^- a/\sigma$, as a function of the specific surface area per unit charge, e/σ, for different ion sizes. The PB result is plotted with the first layer width taken as 5 **r**A. The 1:z electrolyte bulk concentration is $c_b = 1m$M and the valency $z = 4$.
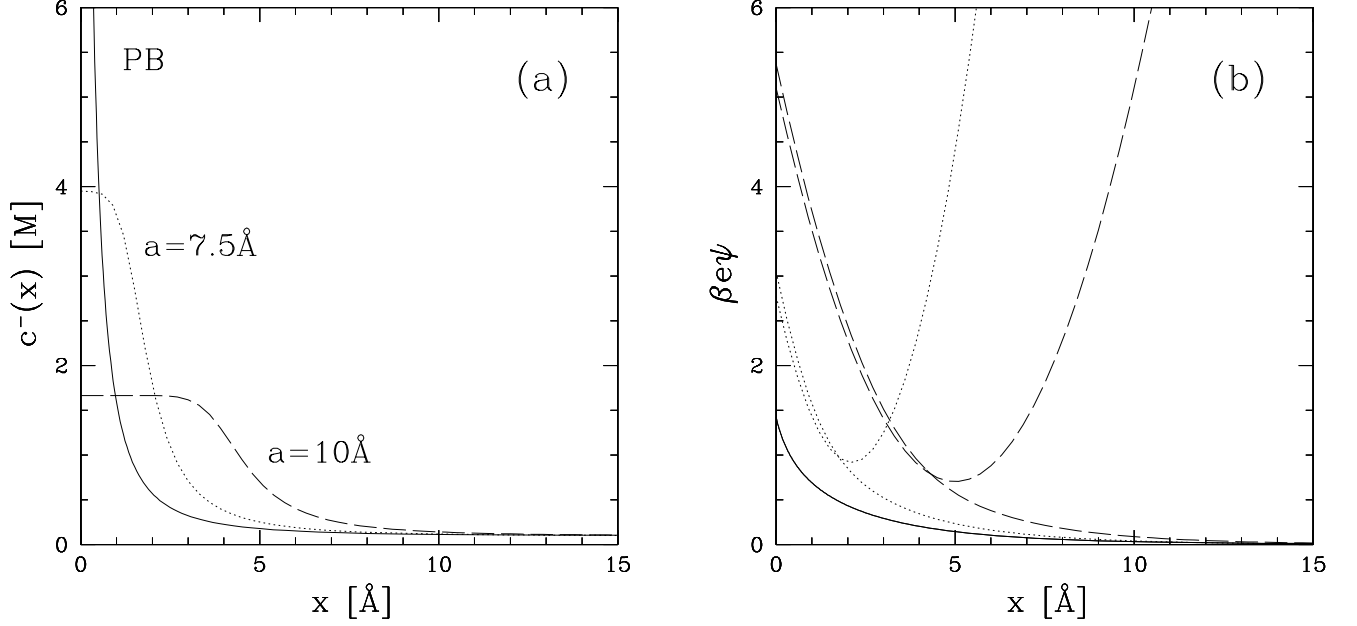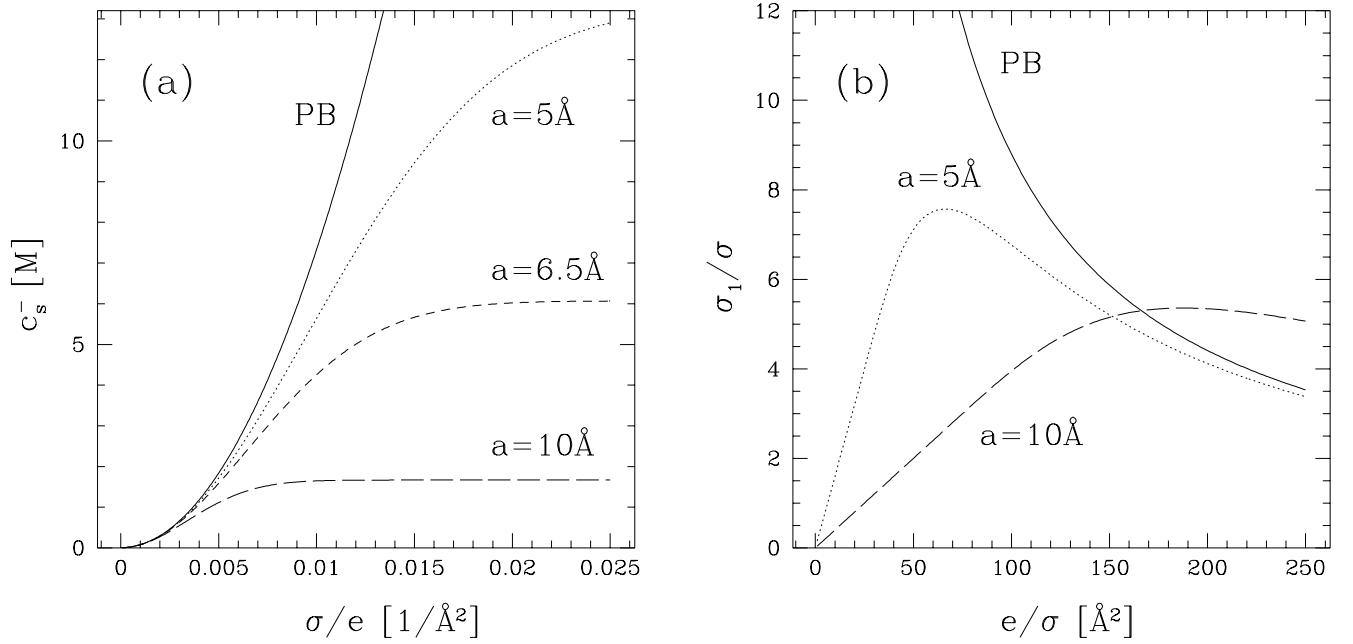

Fig. 1

Fig. 2